

Preliminary Results of NASA Lithium-Ion Cell Verification Testing for Aerospace Applications

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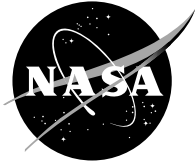
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This report contains preliminary findings, subject to revision as analysis proceeds.

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A Lithium-ion Verification and Validation Program has been established as part of the NASA Aerospace Flight Battery Systems Program. The purpose of this program is to assess the capabilities of current aerospace lithium-ion cells to perform in a low-earth-orbit (LEO) regime. This program involves extensive characterization followed by LEO life testing at ten different combinations of depth-of-discharge, temperature, and end-of-charge voltage. The test conditions selected for the life tests are defined as part of a statistically designed test matrix developed to determine the effects of operating conditions on performance and life of Li-ion cells. Results will be used to model and predict cell performance and degradation as a function of test operating conditions. Four cells from each vendor are being tested at each specific combination of conditions. Conditions included in the test matrix are depth-of-discharges of 20%, 30%, 35%, and 40%; temperatures of 20°C, 30°C, and 40°C; and end-of-charge voltages of 3.85 V, 3.95 V, and 4.05 V. Cells are randomly assigned to packs and packs are randomly assigned to test conditions. The test regime involves periodic capacity measurements to 3.0 V at the conditions of the test. Cells are being evaluated in 4-cell series strings with charge voltage limits being applied to individual cells. Individual cell control is provided via charge control units designed and built at NASA Glenn Research Center that bypass excess current once a cell has reached the desired end-of-charge voltage. Testing is being performed at the Naval Surface Warfare Center/Crane Division in Crane, IN. Testing was initiated in September 2004 with 40 Ah cells from Saft and 30 Ah cells from Lithion. The test program is being expanded with the addition of cells from Mine Safety Appliances Co. (MSA) and the addition of modules from AEA Technology composed of 18650 cells. Preliminary results showing voltage, temperature, available discharge capacity at the test conditions per unit mass, and voltage dispersion as they change over time are presented.

Nomenclature

<i>C</i>	= cell capacity
<i>DOD</i>	= depth-of-discharge
<i>EOCV</i>	= end-of-charge voltage
<i>LEO</i>	= low-earth-orbit

I. □ Introduction

Rechargeable lithium-ion batteries offer a 2-3 times improvement in specific energy and energy density with a wider operational temperature range as compared to nickel-based battery technology. While lithium-ion technology has been successfully used in both planetary rovers and on geosynchronous satellites, its long-term cycle life at low-earth-orbit (LEO) cycling conditions has not been validated. In addition, differences in battery performance caused by operating conditions, vendor-specific designs, and ongoing technology developments need to be assessed. The NASA Aerospace Flight Battery Systems Program validates and verifies battery technologies for flight and has initiated long-term cycle life testing to assess the capabilities of current aerospace lithium-ion cells to perform during long-term NASA LEO missions. A flexible program was developed at NASA Glenn Research Center to enable assessment of technology developments as they occur as well as provide information about different cell vendors and cell designs using a statistically designed matrix of test conditions that includes three levels of temperature, end-of-charge voltage, and depth-of-discharge as shown in Table 1.

II. □ Description of Testing

Before the start of life cycle testing, acceptance, characterization, and self-discharge testing are performed. If the cells need to be stored at any point, the manufacturer's recommendations for storage are followed. The testing is being performed at Naval Surface Warfare Center/Crane Division in Crane, IN. For the life cycle testing, the individual cells were electrically connected in packs of four while still mechanically constrained as individual cells so that thermal effects could be minimized.

A. Acceptance and Characterization Testing

After performing a receiving inspection, all cells are cycled at 20°C to determine their capacity with 3 cycles of successive charging at a C/5 rate to 4.1V, followed by a C/10 rate to 4.1 V and a C/50 rate to 4.1 V where the C-rate is based on the nameplate capacity. The cells then stand at open circuit for one hour and are discharged at C/2 to 3.0 V followed by a C/10 discharge to 3.0 V. Two cycles of the same cycling regime are performed on 4 cells from each vendor at -30°C, -10°C, 0°C, 10°C, 20°C, 30°C, 40°C, and 50°C.

B. Determination of Actual Capacity

Actual capacity of the cells is determined by successive charge/discharge cycles at 20°C. Cycles use a C/5 charge to 4.1 V with a taper charge to C/50. Discharge to 3.0 V is completed at C/2. Current is initially based on characterization results for capacity. In successive cycles, the C used to calculate the rates is adjusted so that it is based on the average capacity found in the previous cycle. This is repeated until the change in capacity during the discharge is less than 1%.

C. Self-Discharge Rate Determination

The self-discharge rate in mV/day of all of the cells is then determined at 20°C. The cells are discharged at C/10 to 3.0 V, followed by a stand at open circuit for one hour. The cells are charged at C/10 to 4.05 V with a taper to C/50. The cells then stand for 168 hours at open circuit and the voltage decay is measured. The cells are then discharged at C/10 to 3.0 V.

D. Determination of Capacity at Specific Test Conditions

Before starting life cycle testing, the capacity of the cells at the specific LEO test conditions is measured to 3.0 V. The cells are charged at the charge rate for the given condition to the end-of-charge voltage, with a taper charge to C/50. The cells then stand for 1 hour at open circuit and are discharged at the LEO discharge rate for the given condition to 3.0 V. This capacity is also measured after every 1000 cycles of life testing.

E. Life Cycle Testing

Life cycle testing of forty, Saft 40 Ah, HE54245, G4 chemistry cells and forty, Lithion 30 Ah, INCP/28/154 cells started in September. Four cells from each vendor are being tested at each combination of test conditions. The ten sets of conditions were statistically chosen to enable modeling of the effects of the operating conditions on cycle life and performance. Failure

of a cell was defined to occur when the end-of-discharge voltage went below 3.0 V. Table 1 shows the combinations of conditions chosen for the test, where the superscript 1 indicates conditions specific to Lithion cells and the superscript 2 indicates conditions specific to Saft cells.

Temperature (°C)	End-of-charge Voltage (V)	Depth of Discharge (%)
30	4.05	20
30	3.85	20
10	3.85	20
30	3.95	30
20	3.95	20
10	3.85	40 ¹ /35 ²
20	3.85	30
30	3.85	40 ¹ /35 ²
20	4.05	40 ¹ /35 ²
10	4.05	30

Table 1. Matrix of test conditions

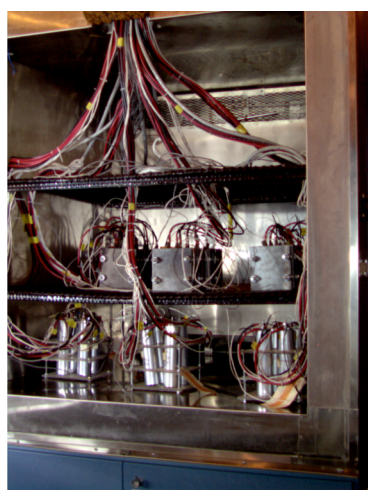


Figure 1. Saft (lower) and Lithion (upper) cells configured in packs in test chamber

For life cycle testing, each cell is charged at a rate that is 1.1 times the rate needed to return the capacity corresponding to the desired depth-of-discharge in 55 minutes until the end-of-charge voltage is reached. The cell is then allowed to taper until a total of 55 minutes of charge have been achieved. The cell is discharged for 35 minutes at a discharge current calculated using the desired depth of discharge. The currents are based on the average actual C/2 capacity of the cells from each vendor that was determined in the capacity measurement.

Cells from each vendor are randomly assigned to packs. Each pack consists of four cells electrically connected in series with voltage limits being applied to the individual cells by charge control units designed and built at NASA Glenn Research Center that bypass excess current once a cell has reached the desired end-of-charge voltage¹. The cells are mechanically restrained as individual cells. The packs are then randomly assigned to a set of test conditions. Testing is being performed in temperature-controlled chambers. Figure 1 shows Saft and Lithion cells configured in packs in one of the test chambers prior to the start of test.

Temperature (°C)	End-of-charge Voltage (V)	Depth of Discharge (%)
30	4.05	40 ¹ /35 ²
10	4.05	20

Table 2. Test conditions at NASA Marshall Space Flight Center

Ah	Saft	Lithion
count	40	40
avg	45.901	32.712
min	45.009	31.833
max	46.396	33.318
range	1.387	1.485
std dev	0.206	0.369
coeff. of variation	0.45%	1.13%

Table 3. Average Ah capacity of the Saft and Lithion cells

Ten cells each from Saft and Lithion are also being tested at the NASA Marshall Space Flight Center at conditions selected to complement the NASA Glenn Research Center testing. Five cells from each vendor are being tested at two sets of conditions. Data from this test will be included in the statistical evaluation. These conditions are shown in Table 2. Only the testing performed at the Naval Surface Warfare Center/Crane Division in Crane, IN will be discussed here.

III. □ Test results and Discussion

F. Characterization Testing

The average actual C/2 capacity of the 30 Ah Lithion cells was 32.7 Ah, which is 9% larger than its nameplate capacity. The average actual C/2 capacity of the 40 Ah Saft

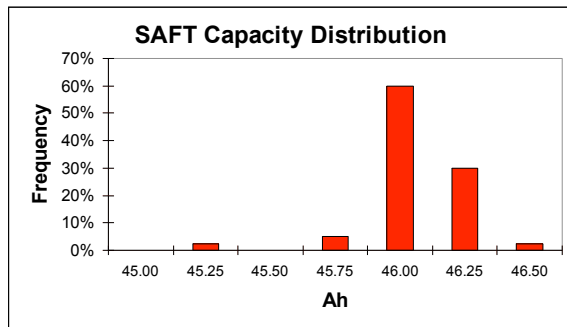


Figure 2. Distribution of Ah capacity for Saft cells

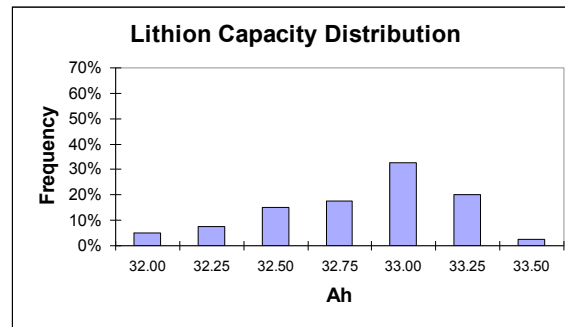


Figure 3. Distribution on Ah capacity for Lithion cells

cells was 45.9 Ah, which is 14.8% larger than its nameplate. Since the differences between actual capacity and nameplate capacity are not consistent between manufacturers, the conditions for the life cycle testing were based on the actual capacities of the cells in order to maintain a consistent basis for comparison of performance. The performance of the Saft cells was more consistent than the performance of the Lithion cells. Table 3 summarizes the statistics for the capacities for the Saft and Lithion cells. Figure 2 shows the distribution of Ah capacity for the Saft cells and Fig. 3 shows the distribution of capacity for the Lithion cells.

Figure 4 shows the Ah capacity of the Lithion and Saft cells over the characterization test temperatures. The Saft cells would not cycle at -30°C.

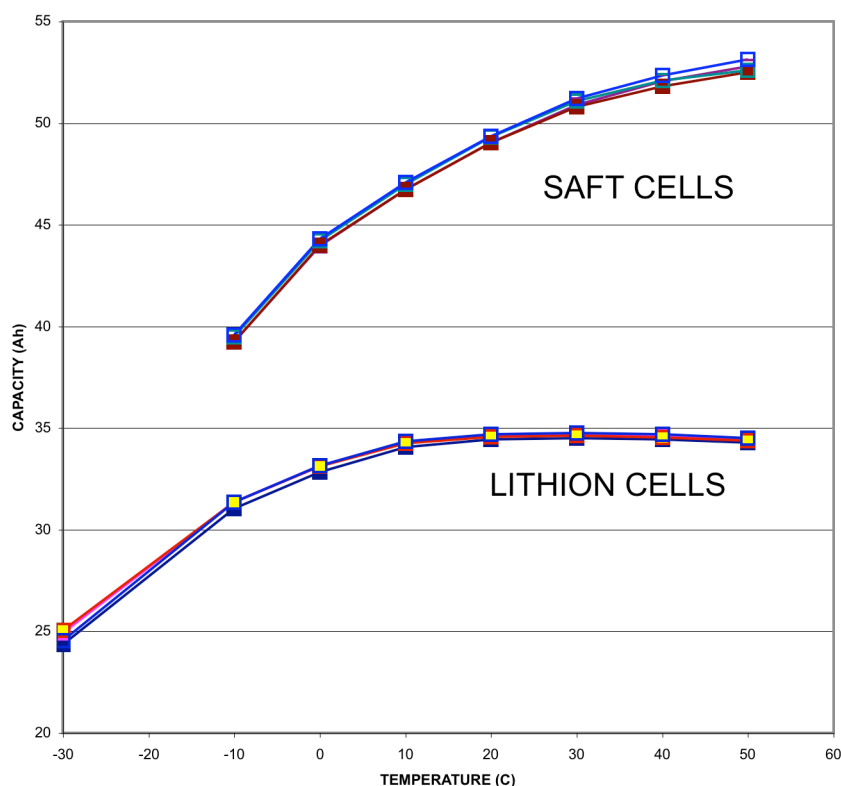


Figure 4 – Ah capacity of Saft and Lithion cells from -30 to 50°C

G. Self-Discharge Rate Determination

Self-discharge rates for the Lithion cells ranged from 0.495 mV/day to 2.710 mV/day. Self-discharge rates for the Saft cells ranged from 0.485 mV/day to 5.496 mV/day. Figure 5 shows the distribution of the self-discharge rates

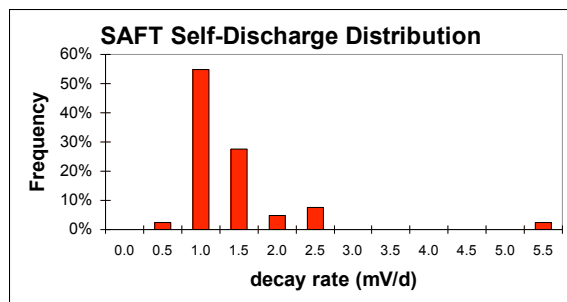


Figure 5. Distribution of self-discharge rate for Saft cells

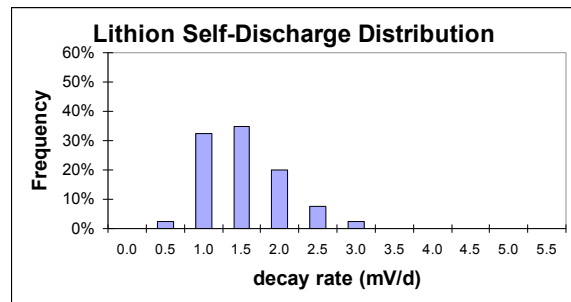


Figure 6. Distribution of self-discharge rate for Lithion cells

mV/d	Saft*	Lithion
count	39	40
avg	0.994	1.292
min	0.485	0.495
max	2.172	2.710
range	1.687	2.215
std dev	0.479	0.481
coeff. of variation	48.22%	37.21%

* with outlier removed

Table 4. Self-discharge rates for the Saft and Lithion cells

Life cycle testing at 30°C started in December 2004 and packs at 30°C have accumulated approximately 3500 cycles as of 01 August 2005. Life cycle testing at 10°C started in January 2005 and packs at 10°C have accumulated approximately 3300 cycles as of 01 August 2005.

Figures 7 through 26 show the end-of-charge and end-of-discharge voltages for the cells in each of the packs at the specific test conditions as a function of the number of cycles. Figures 7 through 12 show results for packs being tested at 20°C. Figures 13 through 20 show results for packs being tested at 30°C. Figures 21 through 26 show results for packs being tested at 10°C.

for the Saft cells and Fig. 6 shows the distribution of the self-discharge rates for the Lithion cells. Table 4 summarizes the statistics for the self-discharge rates for the Saft and Lithion cells. With the removal of one outlier in the Saft cells with a self-discharge rate of 5.496 mV/day, the Saft cells had a slightly smaller average self-discharge rate, but the standard deviation was similar for the Saft and Lithion cells.

H. Life Cycle Testing

Life cycle testing at 20°C started in September of 2004. Packs at the 20°C conditions have accumulated approximately 4800 cycles as of 01 August 2005.

Saft, 3.85 EOCV, 20°C, 30% DOD

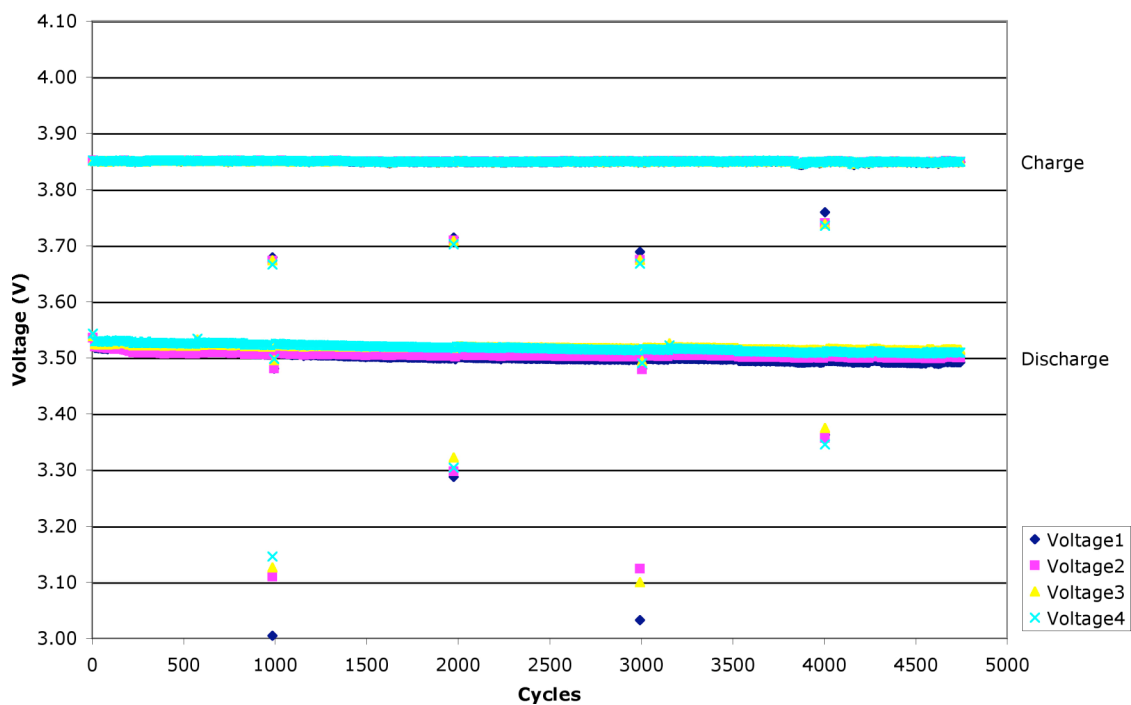


Figure 7. Voltage vs. number of cycles for Saft cells at 20°C, 30% depth-of-discharge, and 3.85 V end-of-charge voltage

Lithion, 3.85 EOCV, 20°C, 30% DOD

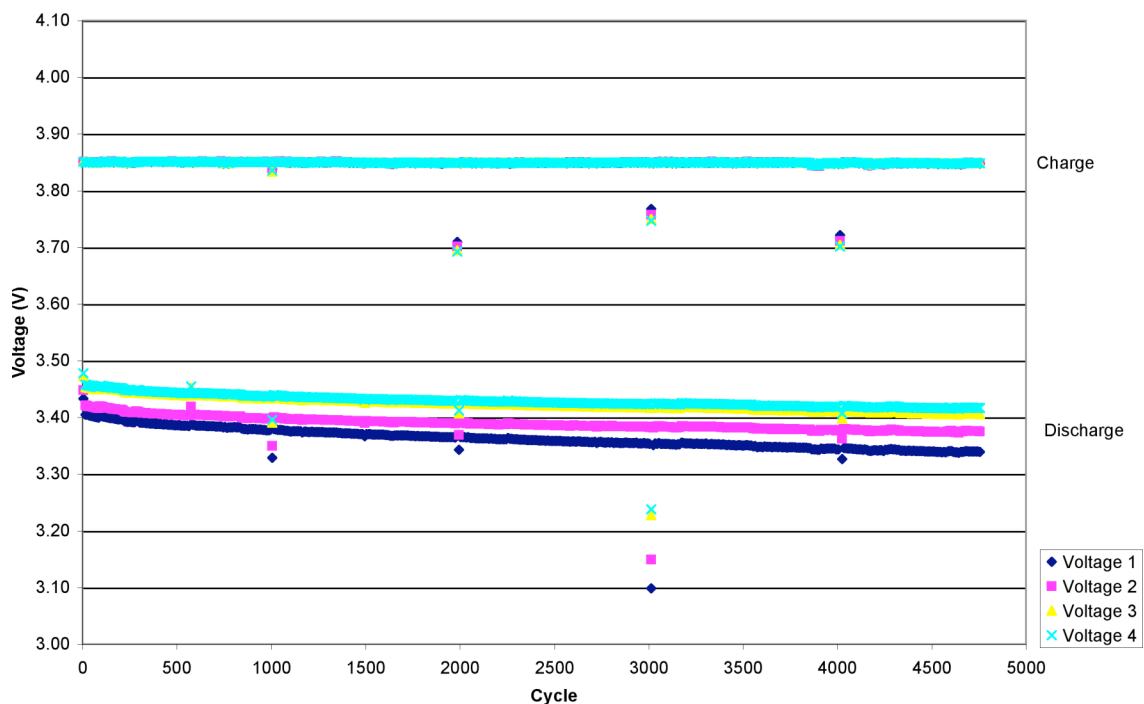


Figure 8. Voltage vs. number of cycles for Lithion cells at 20°C, 30% depth-of-discharge, and 3.85 V end-of-charge voltage

Saft, 3.95 EOCV, 20°C, 20% DOD

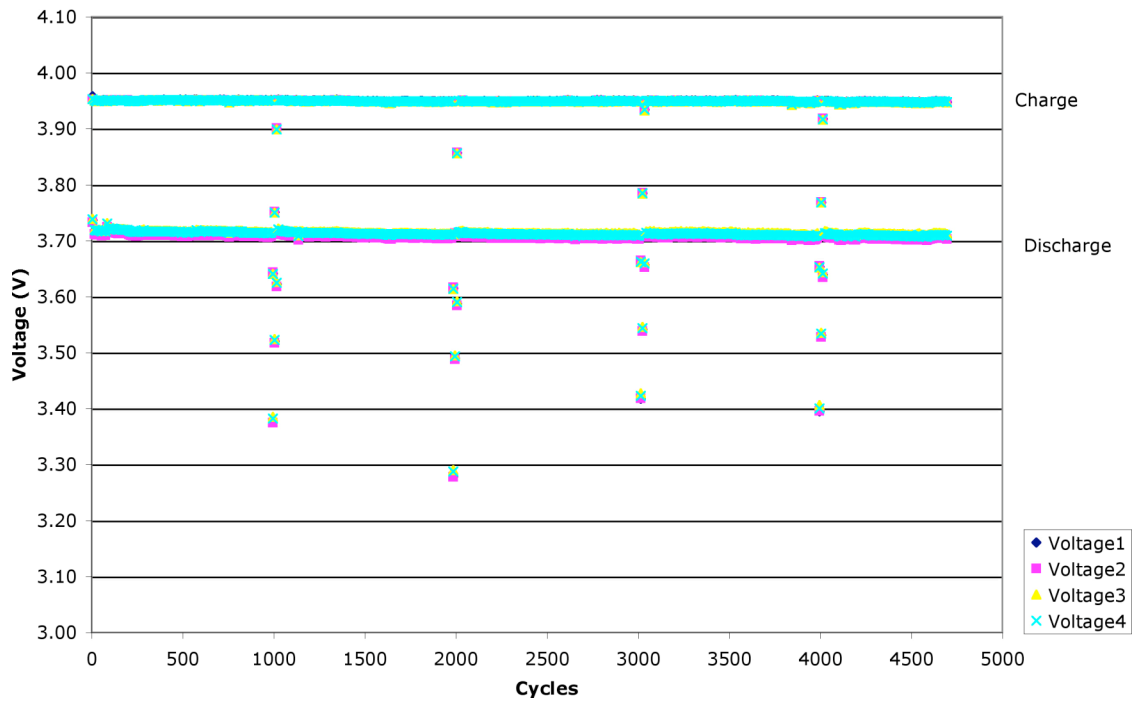


Figure 9. Voltage vs. number of cycles for Saft cells at 20°C, 20% depth-of-discharge, and 3.95 V end-of-charge voltage

Lithion, 3.95 EOCV, 20°C, 20% DOD

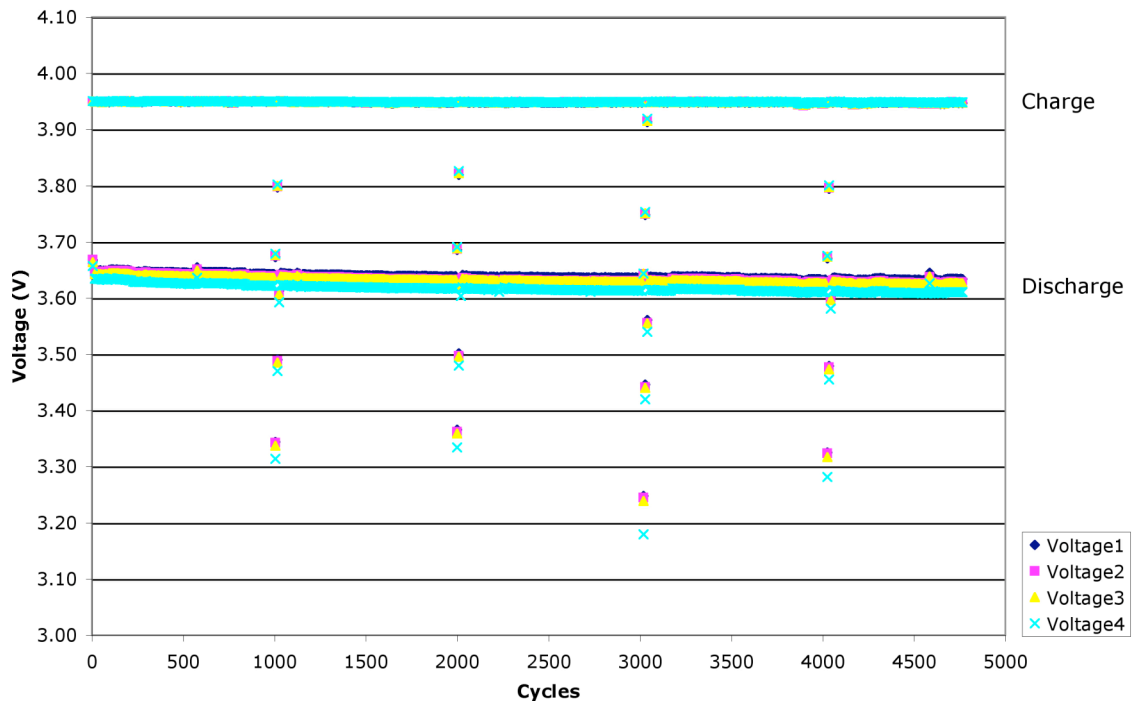


Figure 10. Voltage vs. number of cycles for Lithion cells at 20°C, 20% depth-of-discharge, and 3.95 V end-of-charge voltage

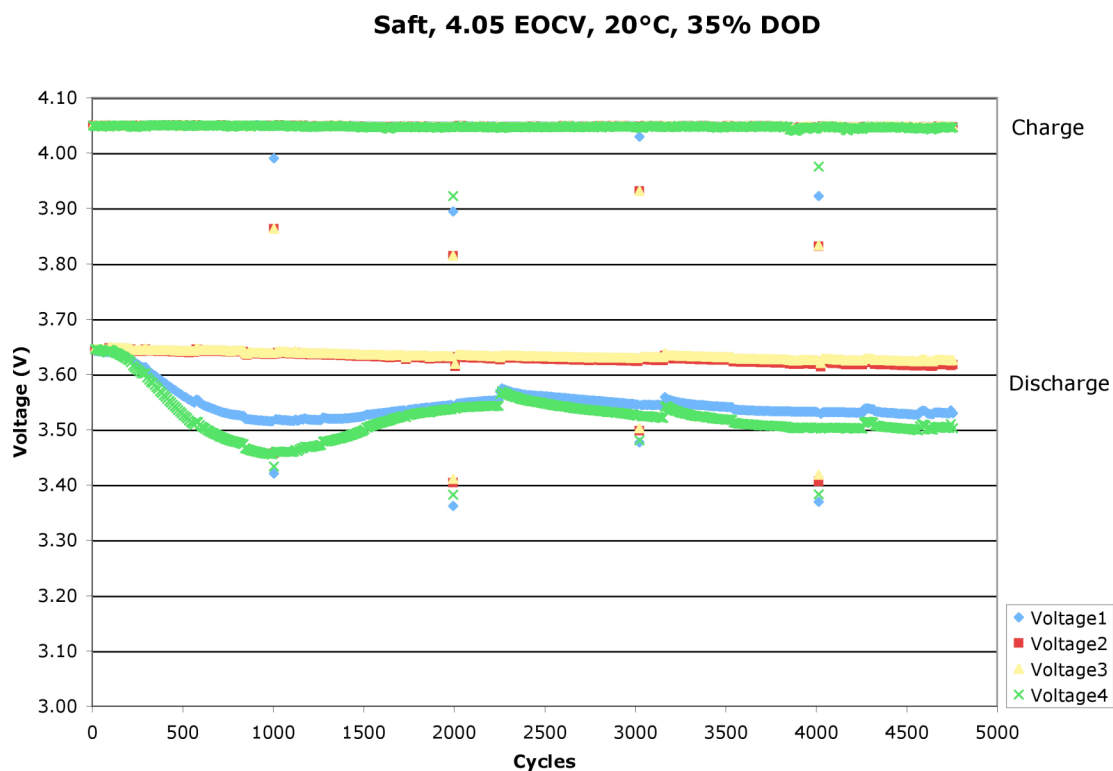


Figure 11. Voltage vs. number of cycles for Saft cells at 20°C, 35% depth-of-discharge, and 4.05 V end-of-charge voltage

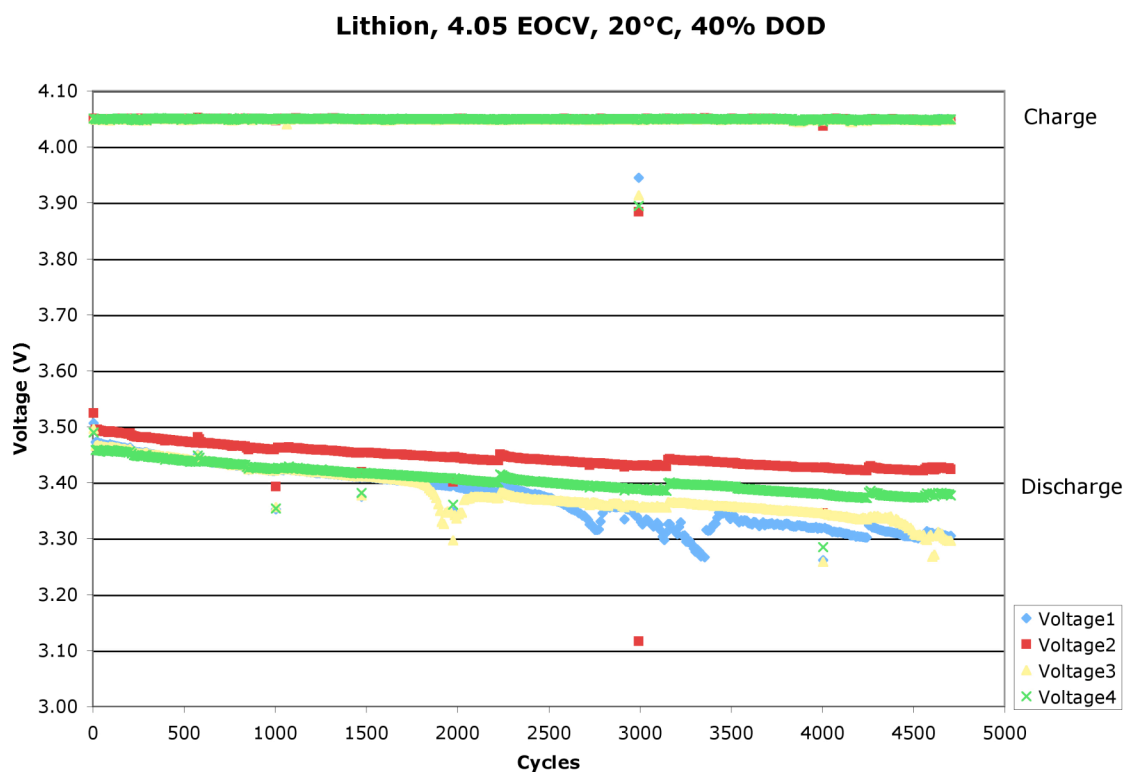


Figure 12. Voltage vs. number of cycles for Lithion cells at 20°C, 40% depth-of-discharge, and 4.05 V end-of-charge voltage

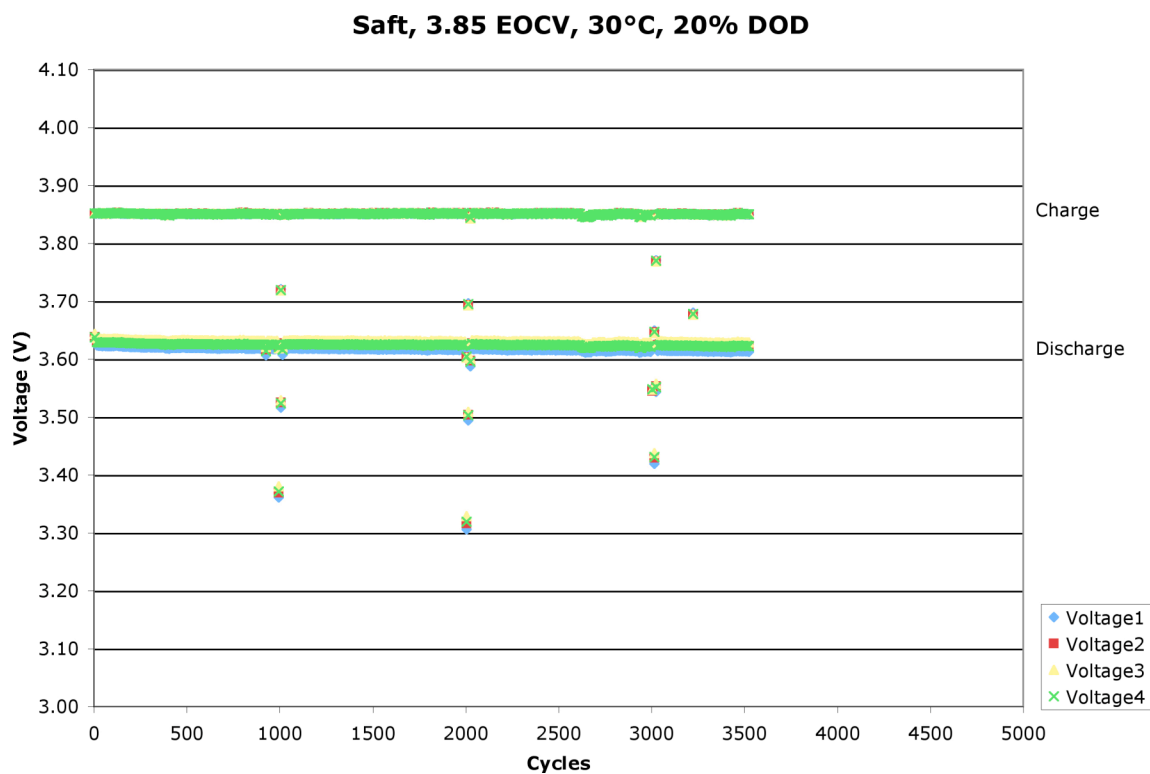


Figure 13. Voltage vs. number of cycles for Saft cells at 30°C, 20% depth-of-discharge, and 3.85 V end-of-charge voltage

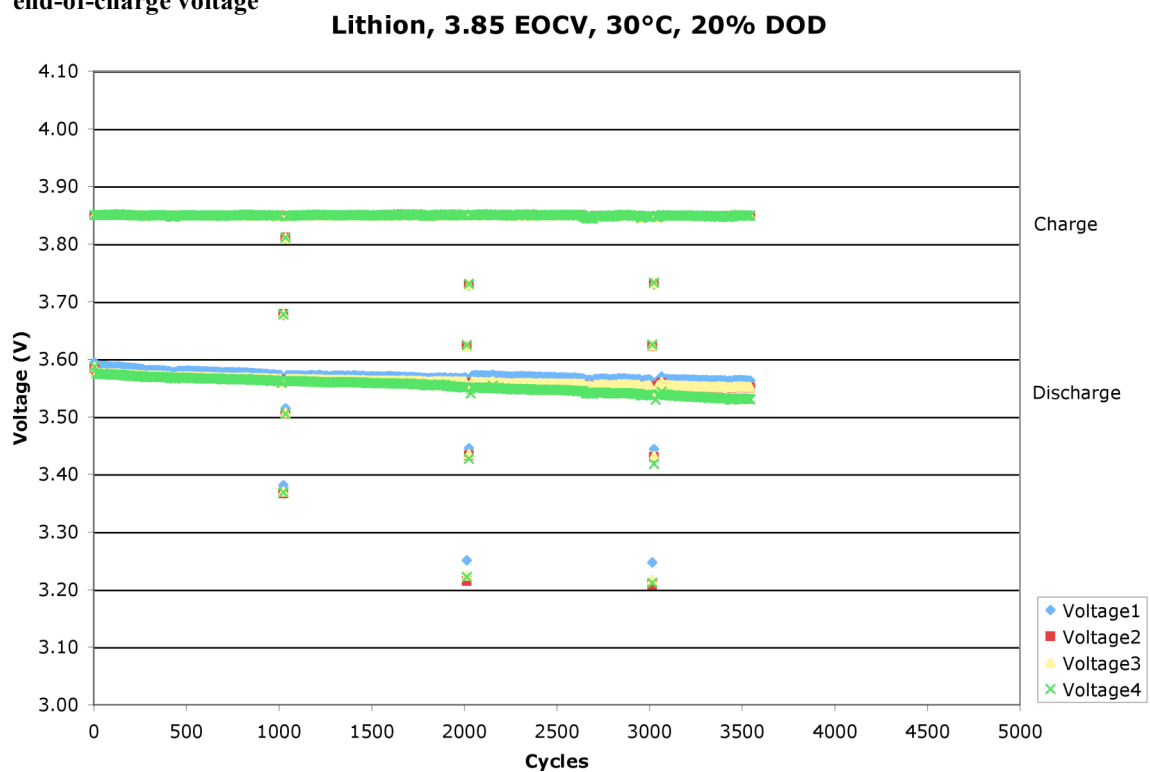


Figure 14. Voltage vs. number of cycles for Lithion cells at 30°C, 20% depth-of-discharge, and 3.85 V end-of-charge voltage

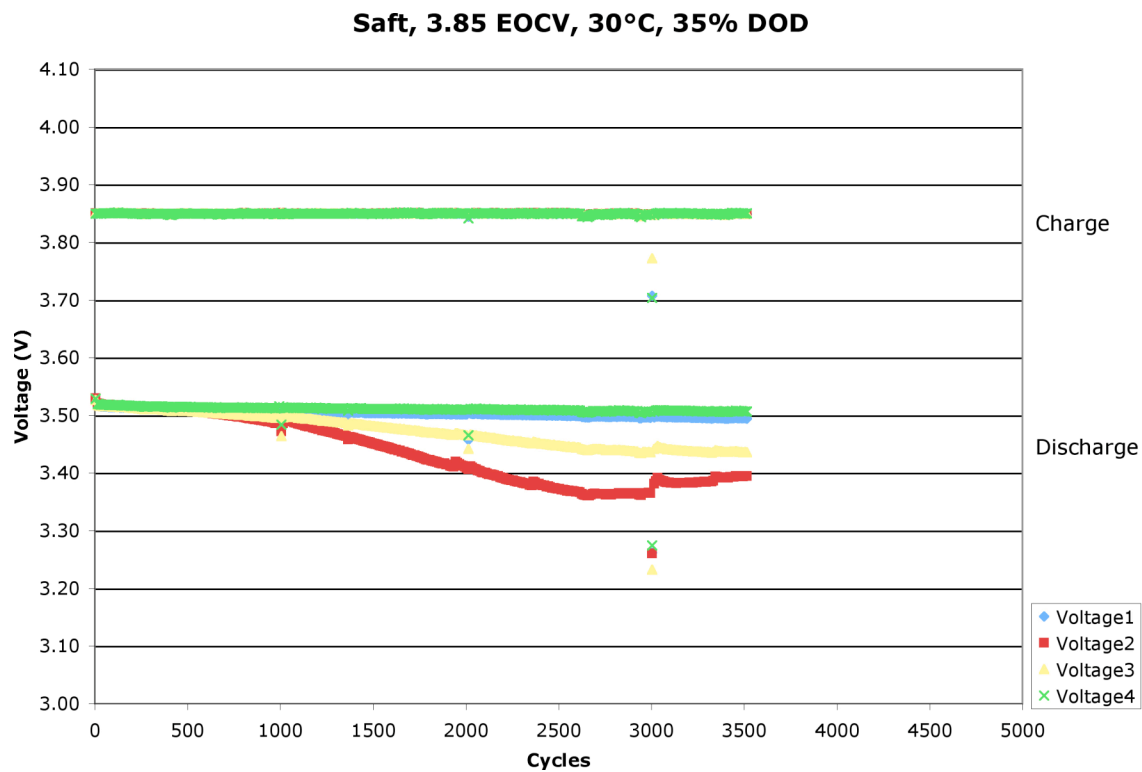


Figure 15. Voltage vs. number of cycles for Saft cells at 30°C, 35% depth-of-discharge, and 3.85 V end-of-charge voltage

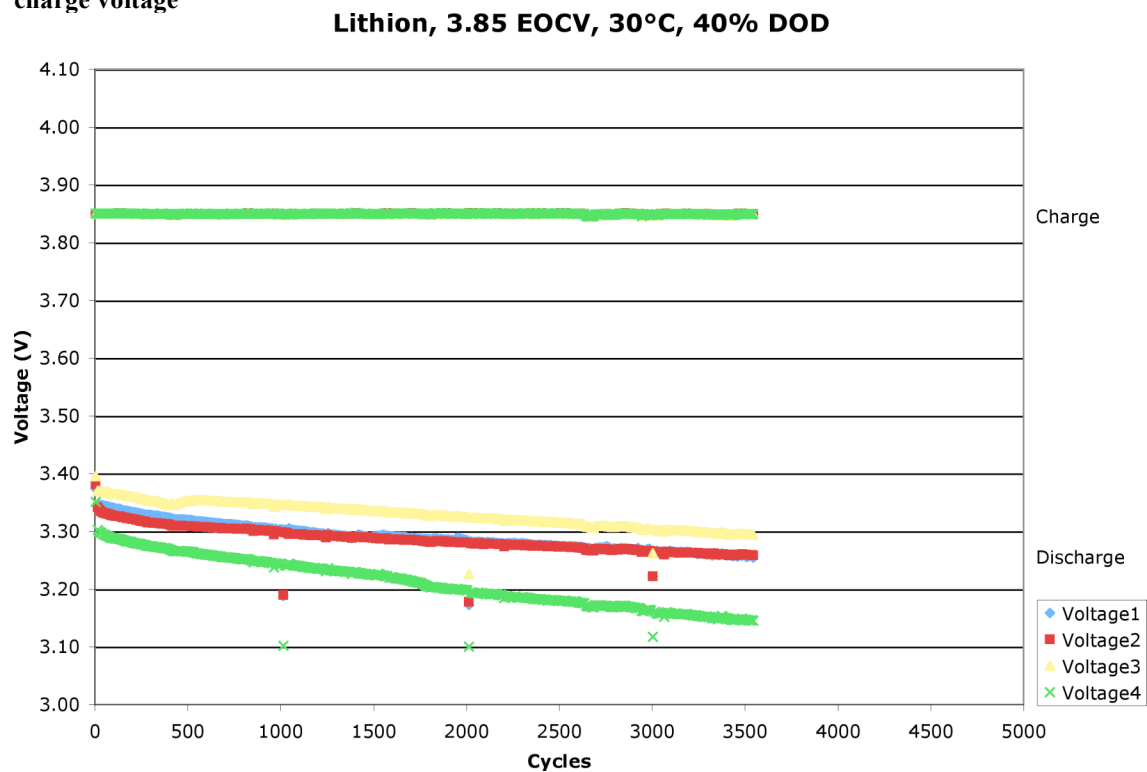


Figure 16. Voltage vs. number of cycles for Lithion cells at 30°C, 40% Depth-of-Discharge, and 3.85 V end-of-charge voltage

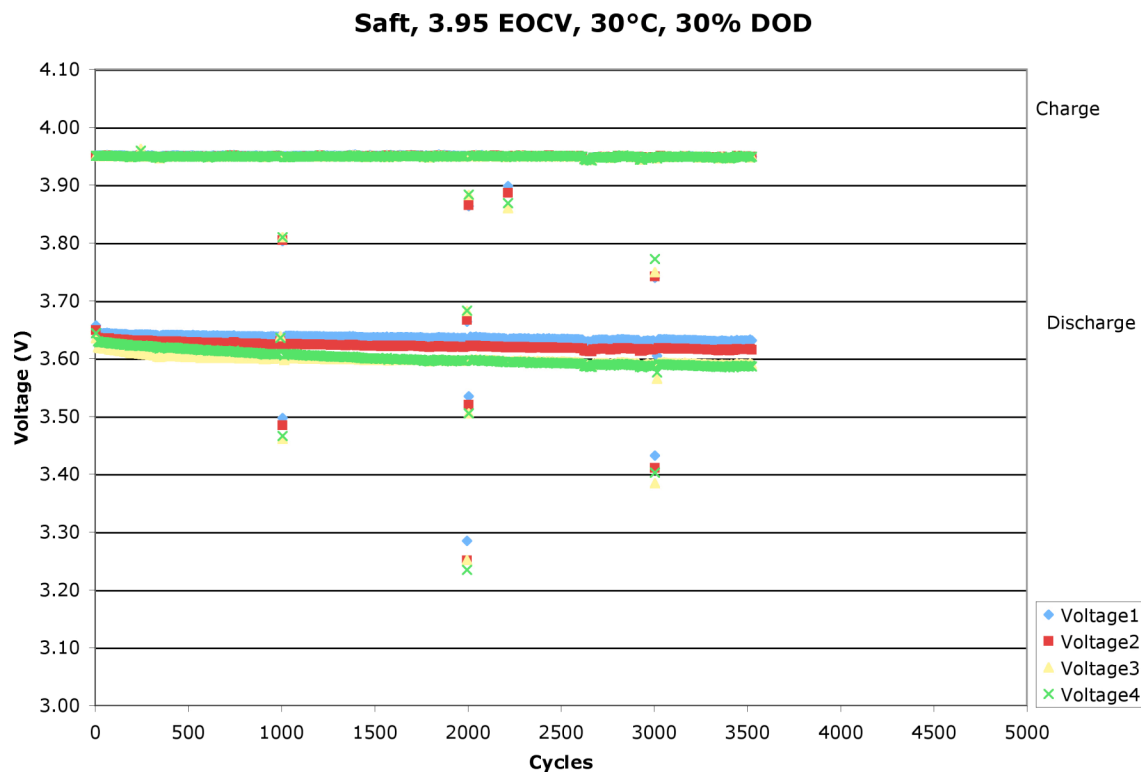


Figure 17. Voltage vs. number of cycles for Saft cells at 30°C, 30% depth-of-discharge, and 3.95 V end-of-charge voltage

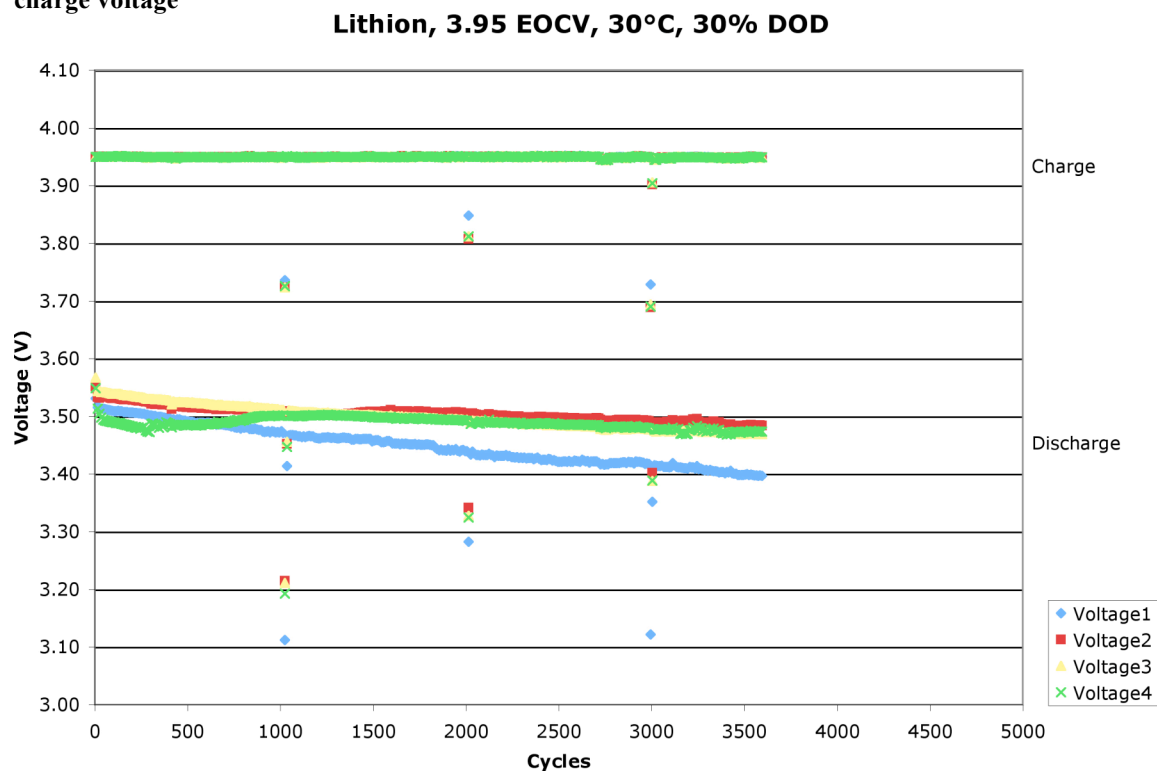


Figure 18. Voltage vs. number of cycles for Lithion cells at 30°C, 30% depth-of-discharge, and 3.95 V end-of-charge voltage

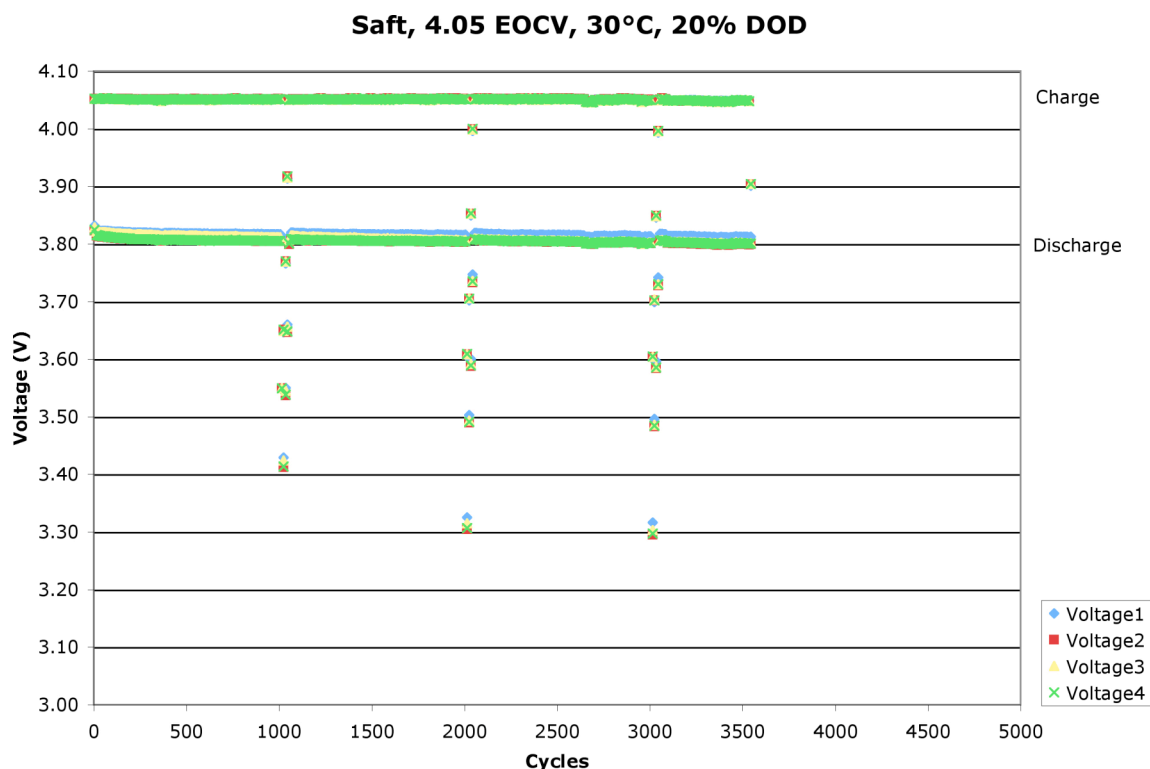


Figure 19. Voltage vs. number of cycles for Saft cells at 30°C, 20% depth-of-discharge, and 4.05 V end-of-charge voltage

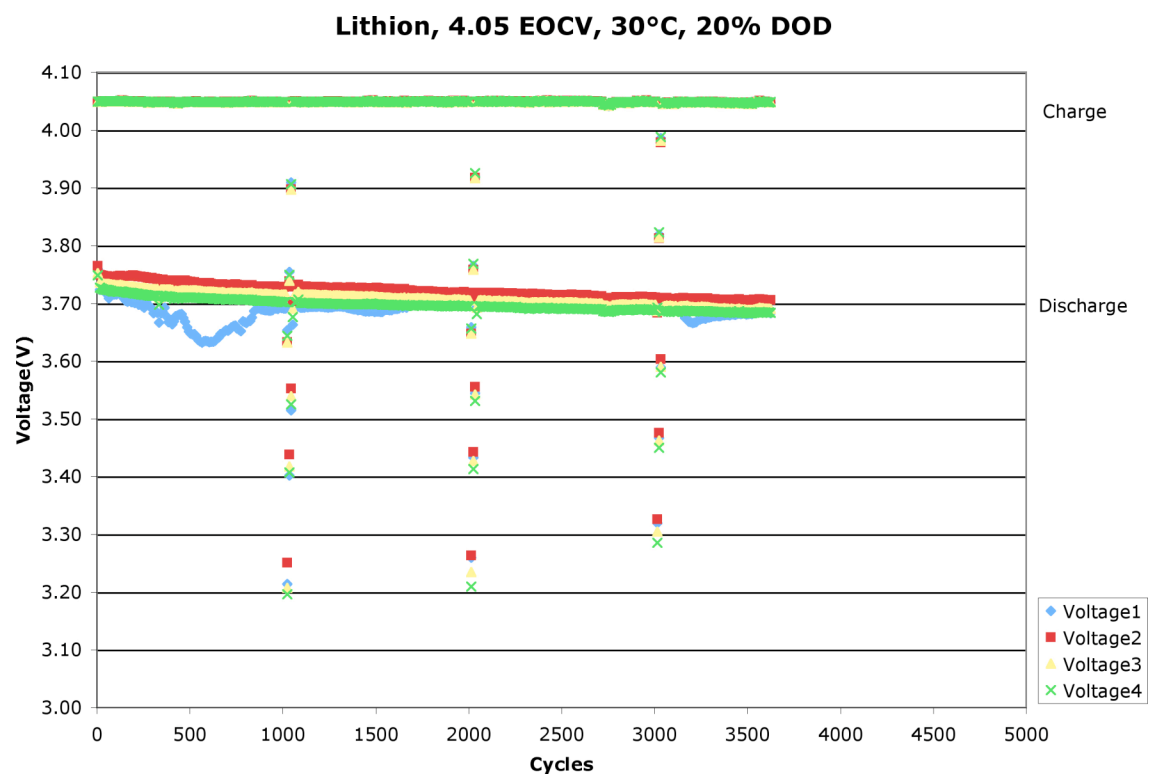


Figure 20. Voltage vs. number of cycles for Lithion cells at 30°C, 20% depth-of-discharge, and 4.05 V end-of-charge voltage

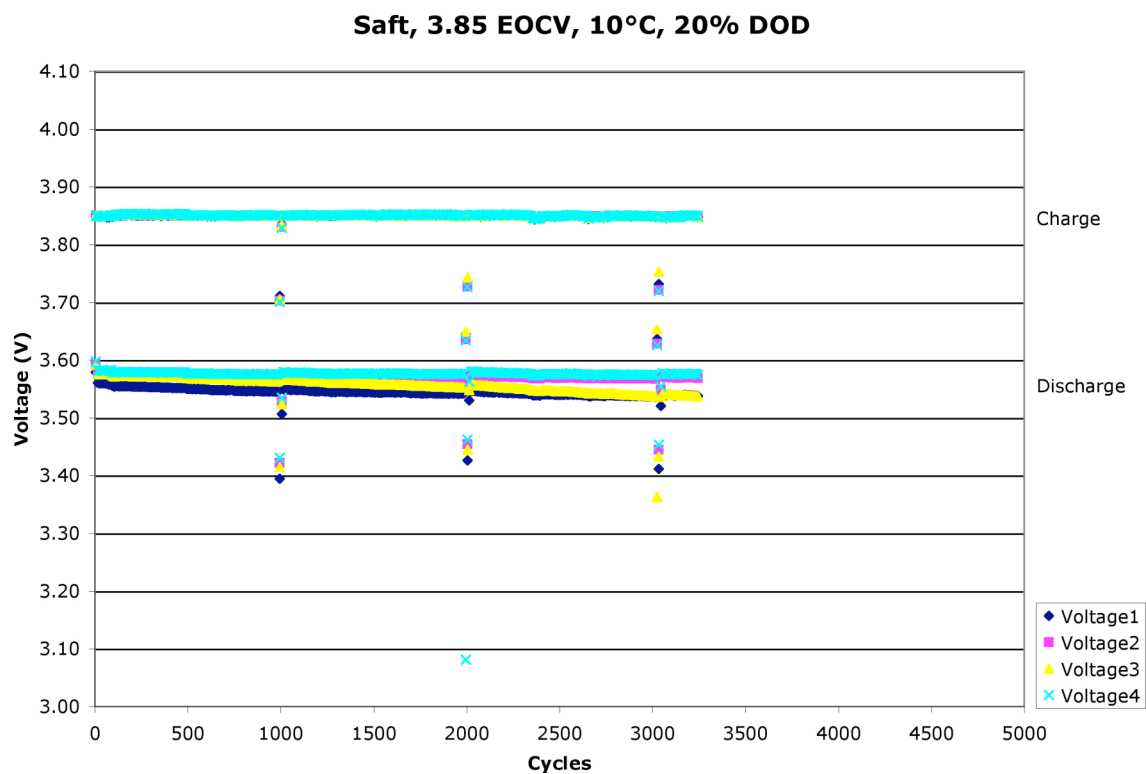


Figure 21. Voltage vs. number of cycles for Saft cells at 10°C, 20% depth-of-discharge, and 3.85 V end-of-charge voltage

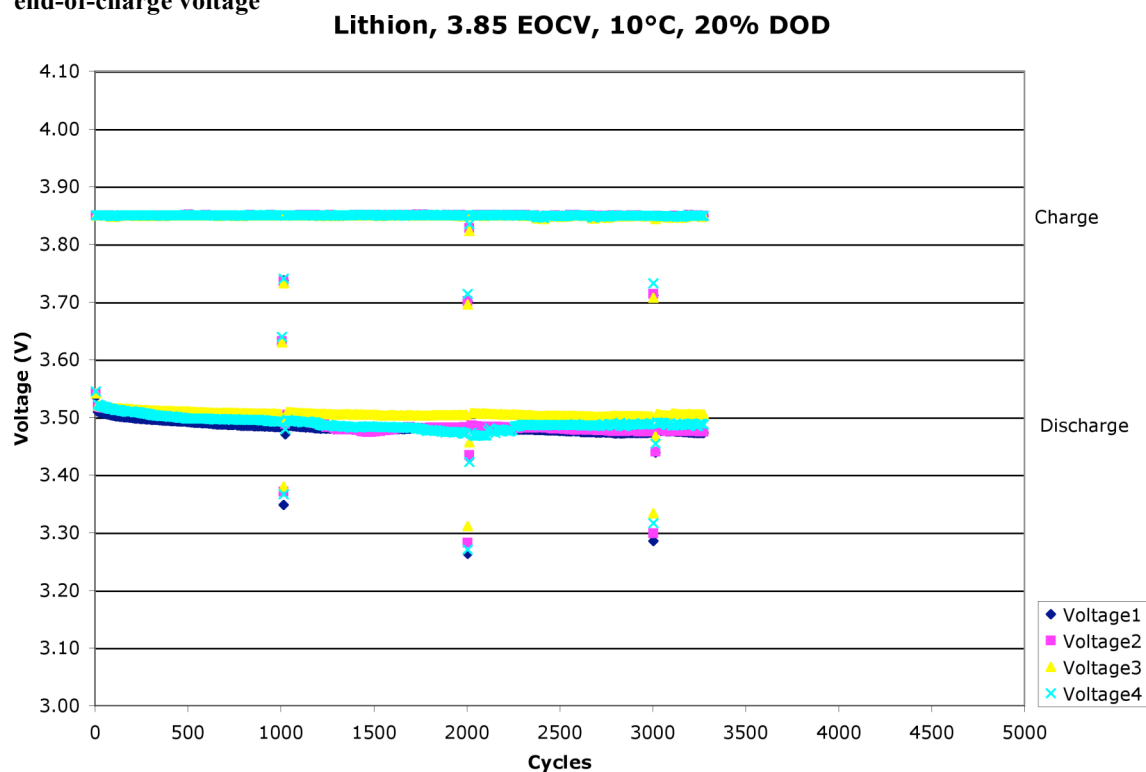


Figure 22. Voltage vs. number of cycles for Lithion cells at 10°C, 20% depth-of-discharge, and 3.85 V end-of-charge voltage

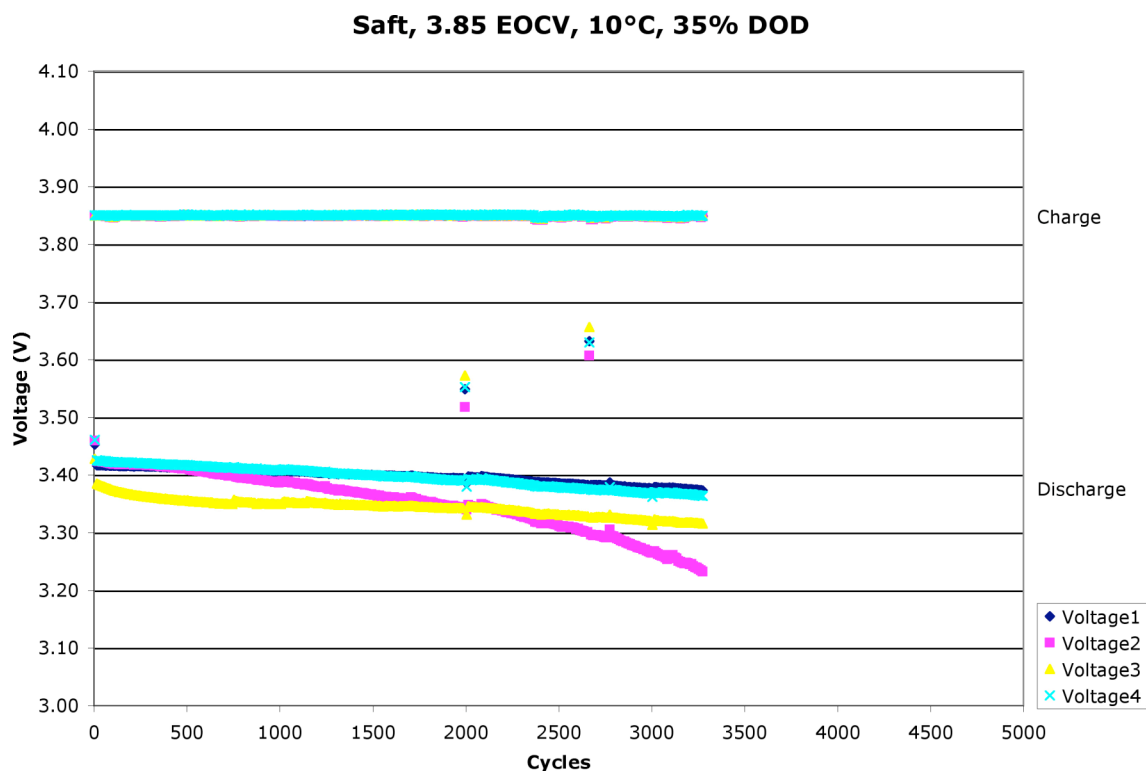


Figure 23. Voltage vs. number of cycles for Saft cells at 10°C, 35% depth-of-discharge, and 3.85 V end-of-charge voltage

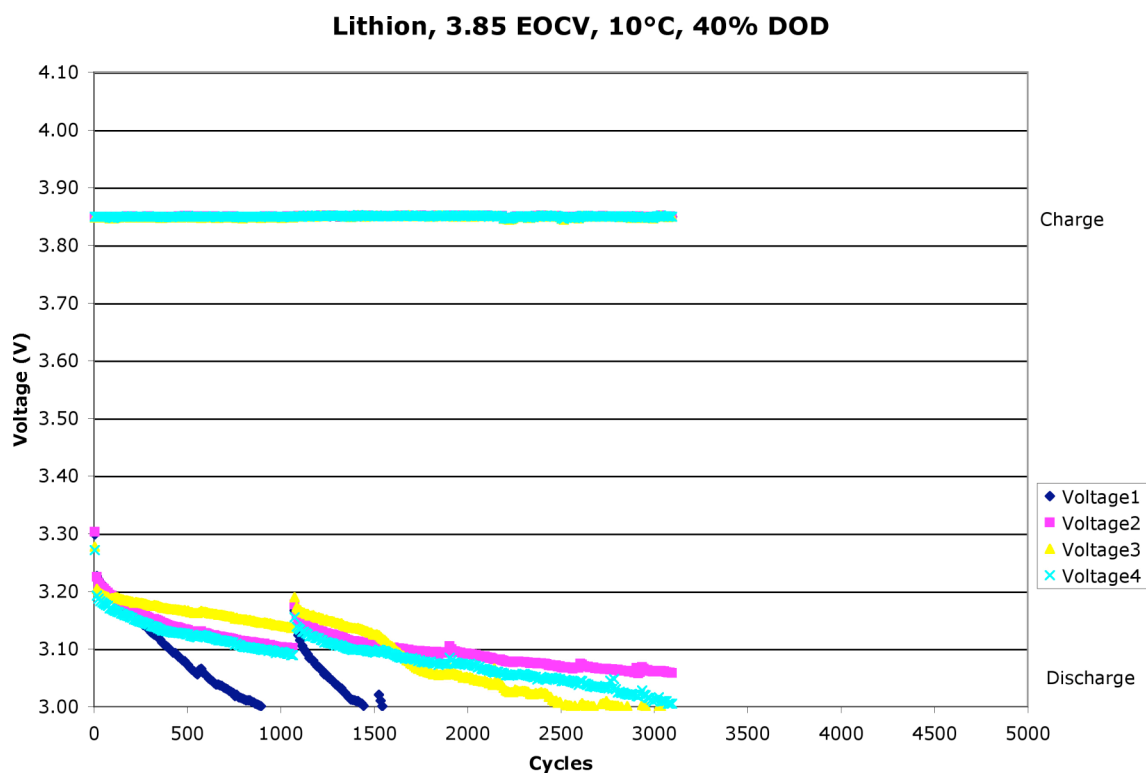


Figure 24. Voltage vs. number of cycles for Lithion cells at 10°C, 40% depth-of-discharge, and 3.85 V end-of-charge voltage

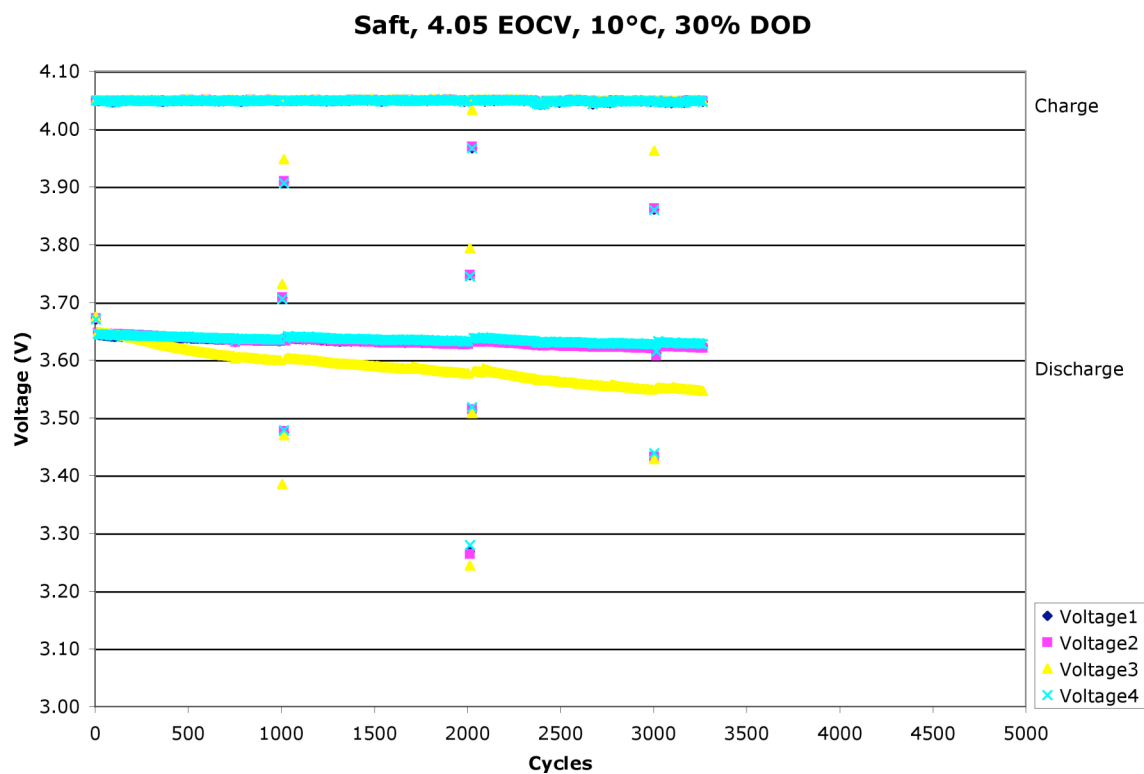


Figure 25. Voltage vs. number of cycles for Saft cells at 10°C, 30% depth-of-discharge, and 4.05 V end-of-charge voltage

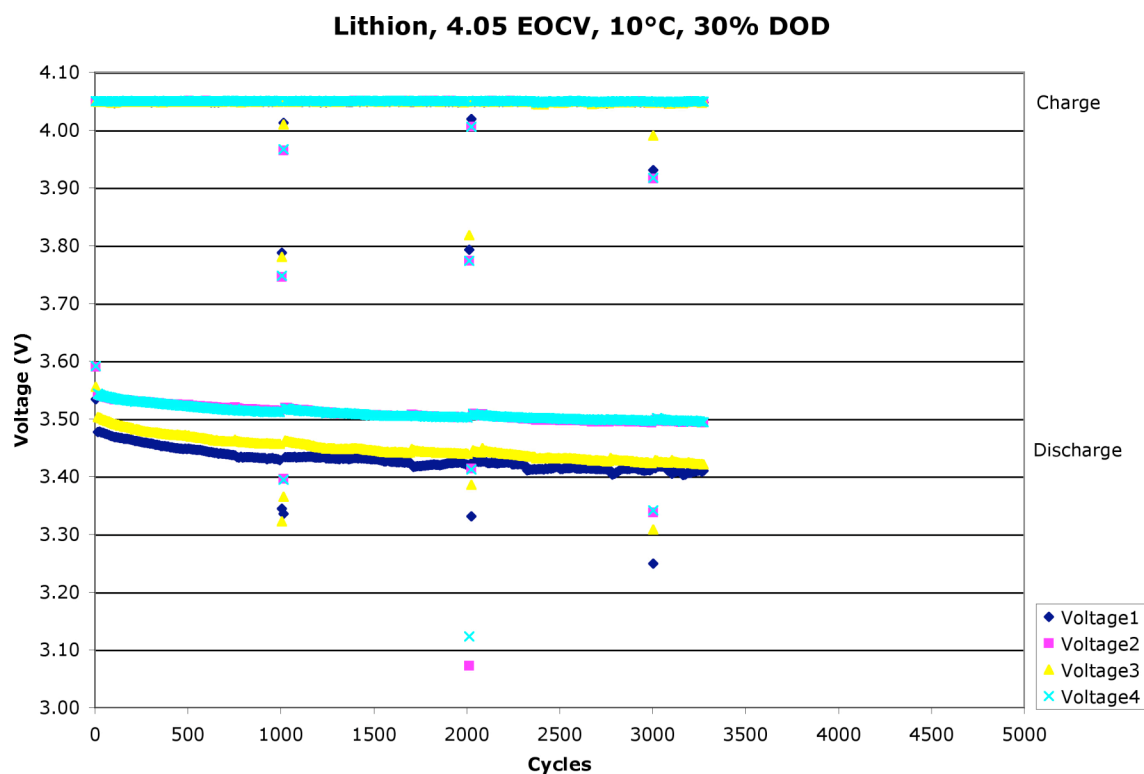


Figure 26. Voltage vs. number of cycles for Lithion cells at 10°C, 30% depth-of-discharge, and 4.05 V end-of-charge voltage

During discharge, cell temperatures vary from 0.2°C for the lowest depth-of-discharge conditions to 2.5°C for the highest depth-of-discharge conditions. The cells with the lowest end-of-discharge voltages in a pack correspond to the warmest cell temperatures in a pack.

The energy delivered by each pack during discharge at the test conditions was calculated as a function of cycles and used to calculate the specific energy of each pack at the given test conditions. Figures 27 through 29 show the specific energy in Wh/kg that each pack is delivering during discharge at the test conditions as a function of the number of cycles. The average specific energy of the Saft cells for a full discharge at C/2 from 4.1 V to 3.0 V at 20°C is 147.7 Wh/kg. The average specific energy of the Lithion cells for a full discharge at C/2 from 4.1 V to 3.0 V at 20°C is 132.7 Wh/kg.

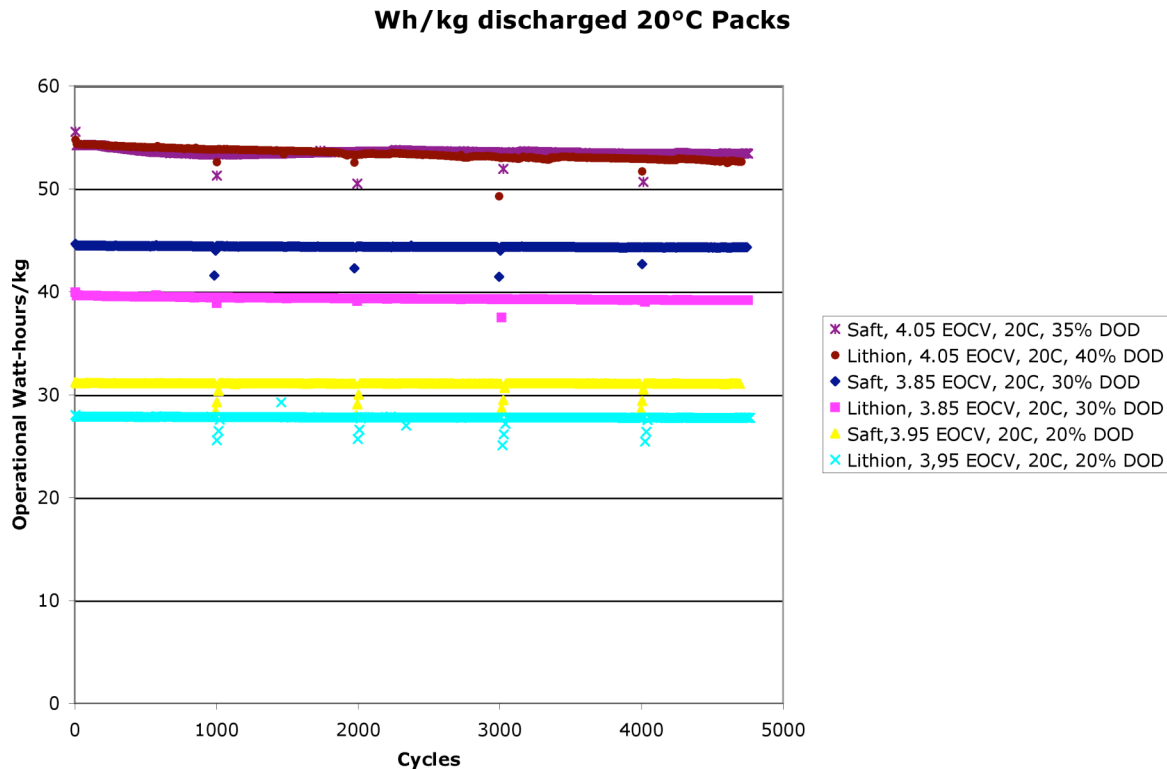


Figure 27. Specific energy delivered by packs tested at 20°C during discharge vs. number of cycles

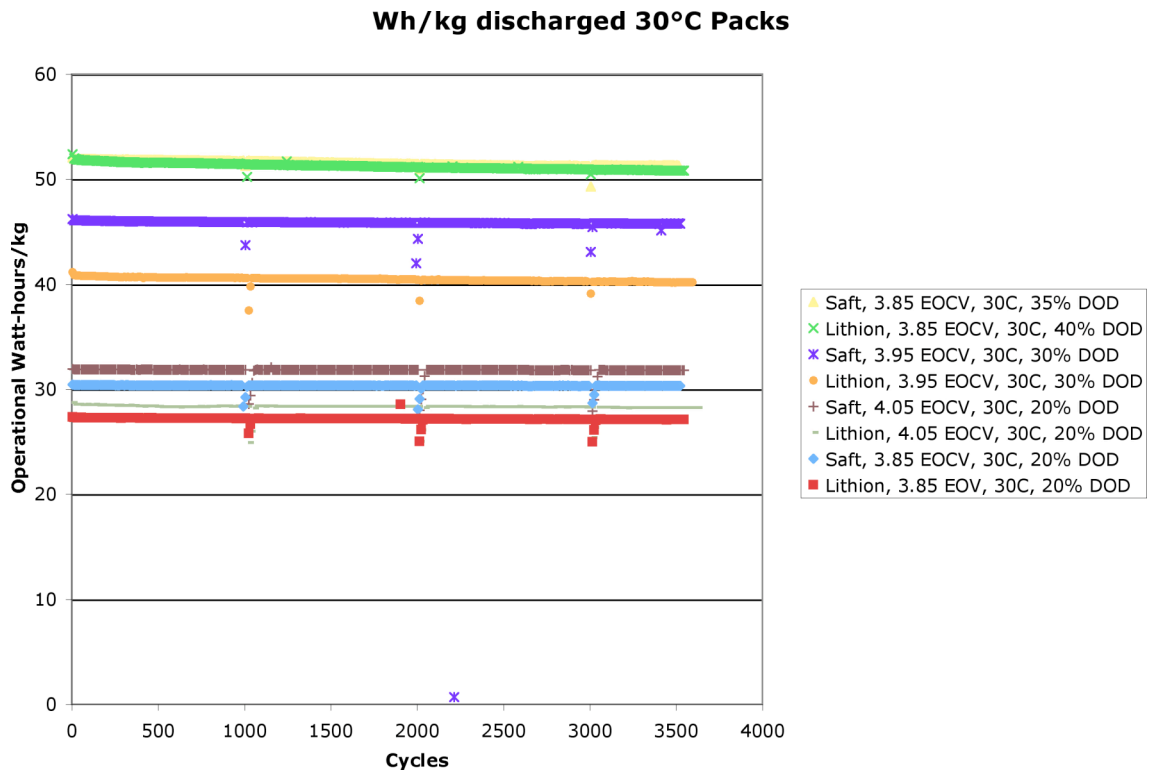


Figure 28. Specific energy delivered by packs tested at 30°C during discharge vs. number of cycles

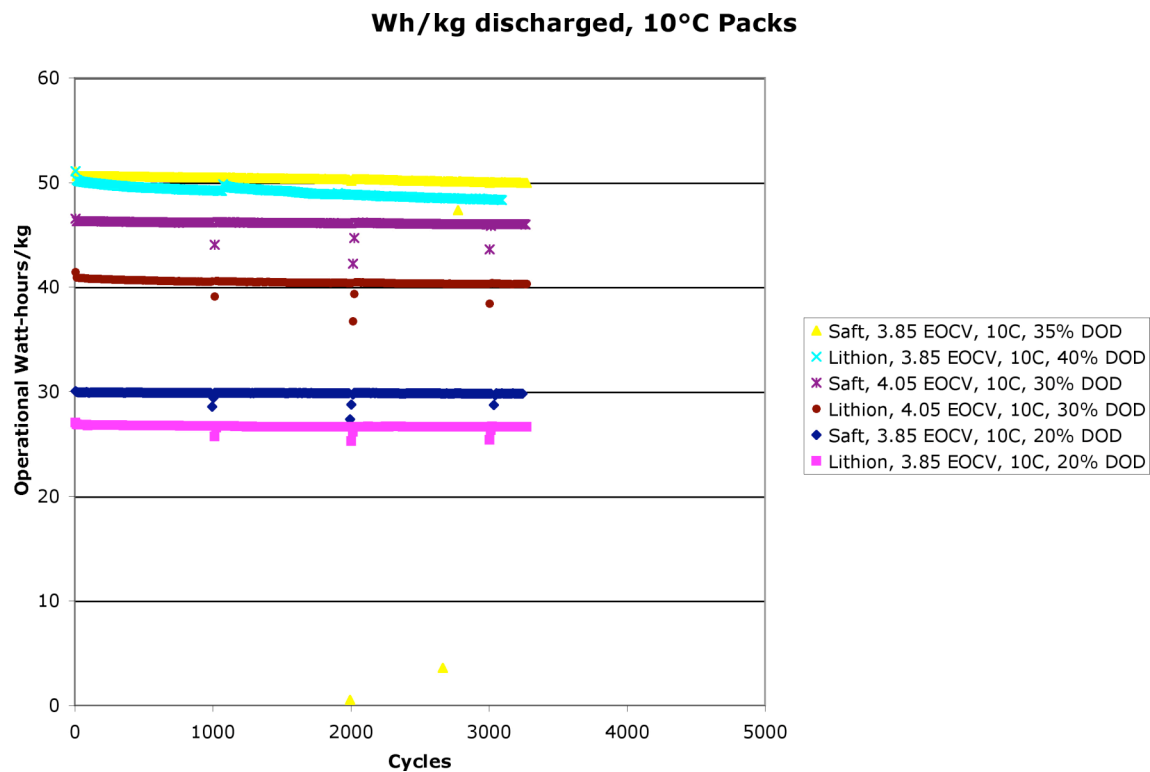


Figure 29. Specific energy delivered by packs tested at 10°C during discharge vs. number of cycles

I. Determination of Capacity at Specific Test Conditions

The discharge capacity of the cells at the specific test conditions is being measured every 1000-cycles as a diagnostic tool. Figures 30, 31, and 32 show these capacities for the cells being tested at 20°C, 30°C, and 10°C respectively. Legend keys correspond to cell serial numbers.

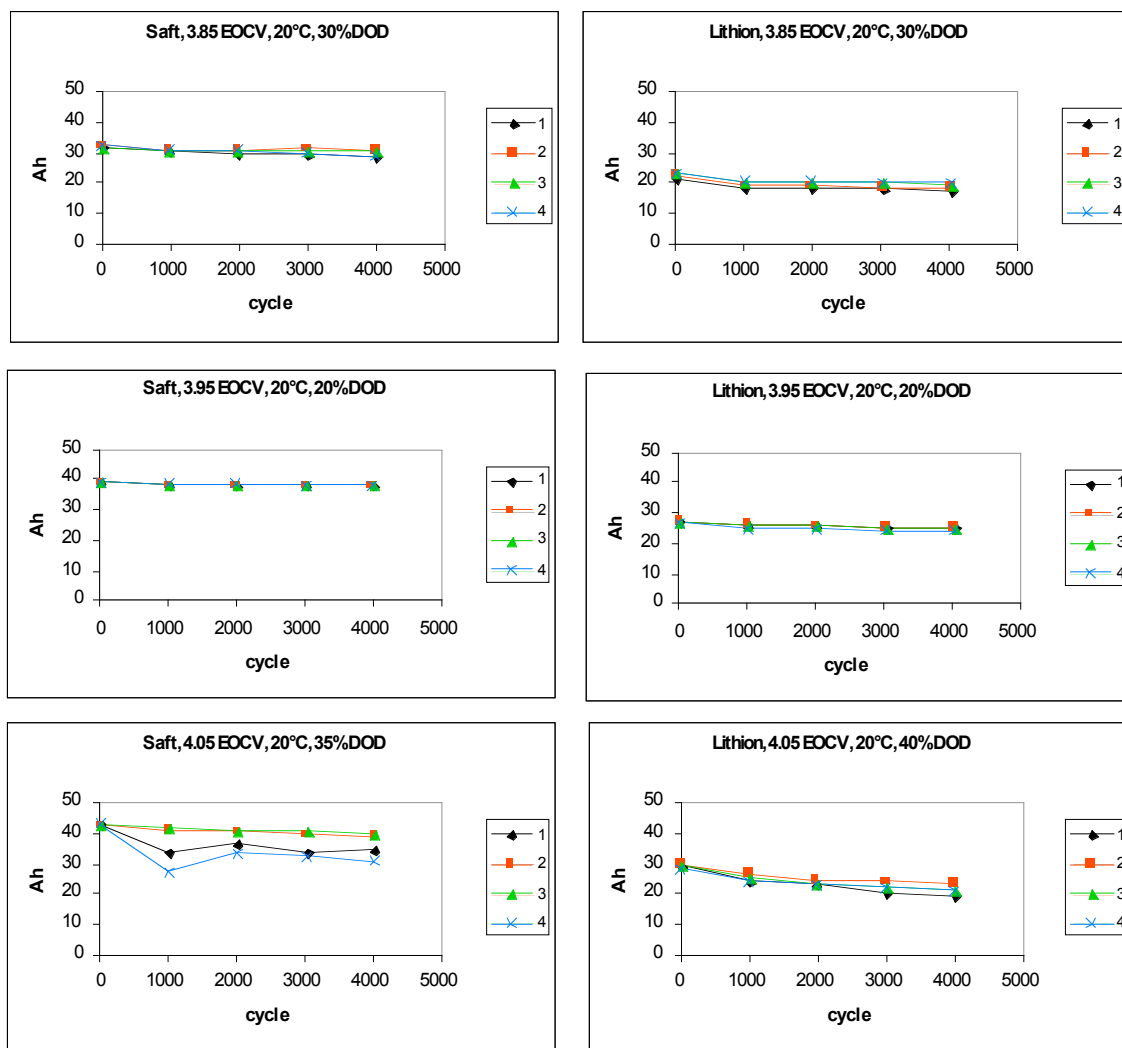


Figure 30. Discharge capacity at test conditions for packs tested at 20°C

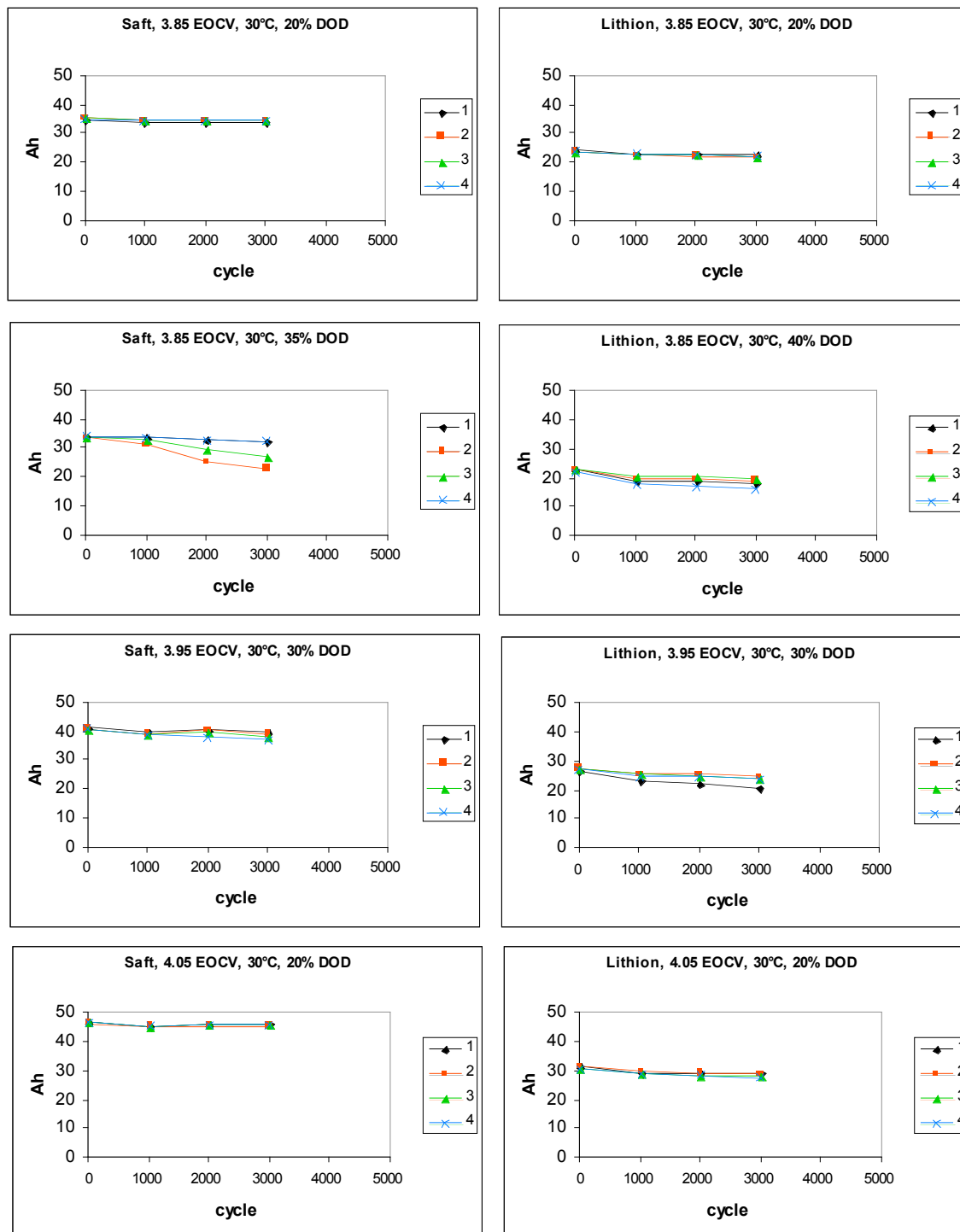


Figure 31 – Discharge capacity at test conditions for packs tested at 30°C

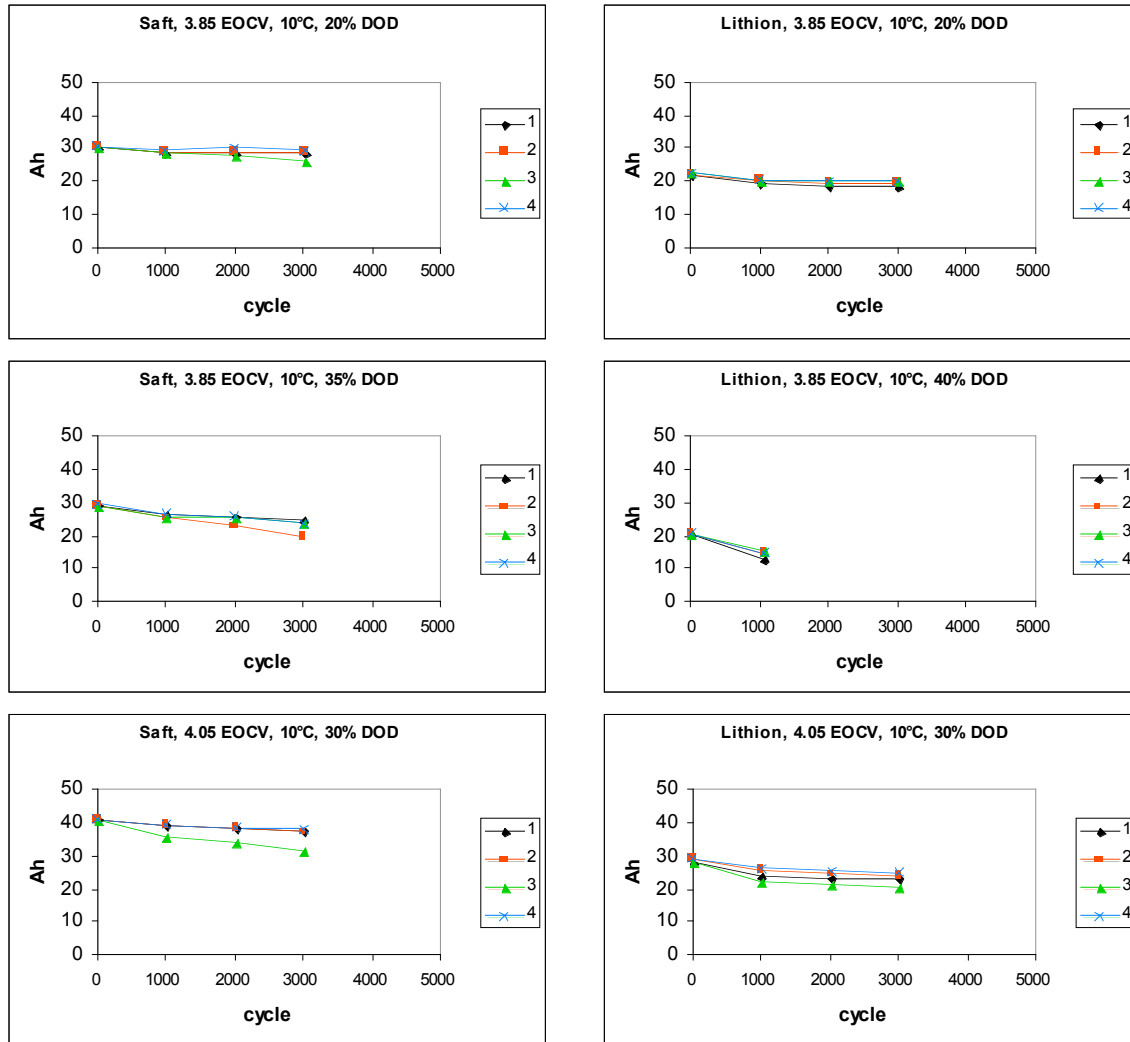


Figure 32 – Discharge capacity at test conditions for packs tested at 10°C

Failure was defined as the point where a cell's end-of-discharge voltage reached 3.0 V. As shown in Fig. 24, one cell has already failed at about 1000 cycles in the Lithion pack running at 10°C with a 3.85 V end-of-charge voltage and 40% depth-of-discharge. This condition combines the lowest end-of-charge voltage in the matrix with the highest depth-of-discharge and the coldest temperature and thus led to the lowest starting end-of-discharge voltages in the test. After failure of one cell, the residual capacity at a C/10 discharge rate was measured. The actual capacity and self-discharge procedures that were performed before life cycling were repeated. The actual capacities at 20°C from 4.1 to 3.0 V ranged from 26.7-30 Ah as compared to 32.6-32.8 Ah before life cycling. The self-discharge rates were found to be 2.07-2.25 mV/day as compared to 0.793 – 1.243 mV/day before life cycling. After this testing, the pack was returned to LEO cycling at the same test condition to see if similar trends were observed in the end-of-discharge voltage.

In this test, the performance of the Saft cells has been more consistent than the performance of the Lithion cells with less variation in voltage between the cells in a pack. In addition, the specific energies of the Saft cells at equivalent test conditions are higher than those of the Lithion cells. Greater decline and more variation in end-of-discharge voltage has been seen in packs with higher depth-of-discharges and in packs with lower chamber temperatures. Trends in the periodic 1000 cycle discharge capacity at the test conditions correlate well with end-of-discharge voltage in LEO cycling and with cell operational temperatures. Cells with low periodic 1000 cycle discharge capacity at the test conditions also tend to exhibit lower end-of-discharge voltage and higher cell

temperatures as compared to the chamber temperature. This result suggests that these weaker cells are experiencing an irreversible capacity loss. Trends in self-discharge rate do not correlate with trends in end-of-discharge voltage or discharge capacity at the test conditions.

The measurement of discharge capacity at the test conditions that is performed every 1000 cycles proves to have a greater effect on the cells with the lowest end-of-discharge voltages. During this procedure, these cells are removed from the circuit as they reach the 3.0 V end-of-discharge minimum on discharge and allowed to stand at open circuit while the remainder finish their discharge to 3.0 V. After these cycles, the cells that were held for a longer time at open circuit reach the end-of-charge voltage sooner and spend a longer time in the taper portion of the charge.

Due to the statistical design of the test matrix, it is hard to perform a direct comparison of pairs of results (except for a comparison across vendors) at specific test conditions since only a few of the conditions are only different in one variable. These results are preliminary results at an early stage in the testing. As more data is accumulated, it will be used to statistically model and predict the effects of temperature, end-of-charge voltage, and depth-of-discharge on cycle life and performance.

IV. □ Future planned work

Life cycle testing is continuing and the data is being evaluated to determine the impacts of the test conditions on end-of-discharge voltage trends. Equations are being developed to describe the trends and will be used to develop a model to predict cycle life.

Forty Mine Safety Appliances 50 Ah cells and 20 AEA Technology modules made from 18650 cells with 4 cells in each series string and 2 strings in parallel are scheduled to be added to the testing being performed at the Naval Surface Warfare Center/Crane Division in the fall of 2005.

References

¹Reid, Concha, Hand, Evan, Button, Rob, Manzo, Michelle, McKissock, Barbara, Miller, Thomas, Gemeiner, Russel, and Bennett, William, "Lithium-Ion Cell Charge Control Unit", 2004 NASA Aerospace Battery Workshop, November 16-18, 2004

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13. ABSTRACT (Maximum 200 words) A Lithium-ion Verification and Validation Program has been established to assess the capabilities of current aerospace lithium-ion cells to perform in a low-earth-orbit (LEO) regime. This program involves extensive characterization followed by LEO life testing at ten different combinations of depth-of-discharge (20, 30, 35, and 40 percent), temperature (20, 30, and 40 °C), and end-of-charge voltage (3.85, 3.95, and 4.05 V). The test conditions are defined as part of a statistically designed test matrix developed to determine the effects of operating conditions on performance and life of Li-ion cells. Results will be used to model and predict cell performance. The test regime involves periodic capacity measurements to 3.0 V at the conditions of the test. Cells are being evaluated in 4-cell series strings with charge voltage limits being applied to individual cells via charge control units that bypass excess current once a cell has reached the desired end-of-charge voltage. Testing was initiated in September 2004 with 40 Ah cells from Saft and 30 Ah cells from Lithion. Preliminary results showing voltage, temperature, available discharge capacity at the test conditions per unit mass, and voltage dispersion as they change over time are presented.				
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